North Atlantic Deep Water export to the Southern Ocean over the past 14 Myr: Evidence from Nd and Pb isotopes in ferromanganese crusts

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[1] The intensity of North Atlantic Deep Water (NADW) production has been one of the most important parameters controlling the global thermohaline ocean circulation system and climate. Here we present a new approach to reconstruct the overall strength of NADW export from the North Atlantic to the Southern Ocean over the past 14 Myr applying the deep water Nd and Pb isotope composition as recorded by ferromanganese crusts and nodules. We present the first long-term Nd and Pb isotope time series for deep Southern Ocean water masses, which are compared with previously published time series for NADW from the NW Atlantic Ocean. These data suggest a continuous and strong export of NADW, or a precursor of it, into the Southern Ocean between 14 and 3 Ma. An increasing difference in Nd and Pb isotope compositions between the NW Atlantic and the Southern Ocean over the past 3 Myr gives evidence for a progressive overall reduction of NADW export since the onset of Northern Hemisphere glaciation (NHG). The Nd isotope data allow us to assess at least semiquantitatively that the amount of this reduction has been in the range between 14 and 37% depending on location. *INDEX TERMS:* 4267 Oceanography: General: Paleoceanography; 4283 Oceanography: General: Water masses; 4825 Oceanography: Biological and Chemical: Geochemistry; 4870 Oceanography: Biological and Chemical: Stable isotopes; 4875 Oceanography: Biological and Chemical: Trace elements; *KEYWORDS:* ocean circulation, water masses, North Atlantic Deep Water, Southern Ocean, radiogenic isotopes, ferromanganese crusts

1. Introduction

1.1. History of Atlantic Ocean Circulation

[2] The strength of the global thermohaline circulation, which is to a large extent controlled by the intensity of NADW production in the Norwegian-Greenland and Labrador Seas, is responsible for the ventilation of the deep ocean and for the meridional heat transport around the globe. Changes in the intensity of NADW production in the past thus had significant consequences for global ocean circulation and climate. The main tools for reconstructing past circulation of the ocean have been stable carbon isotope ratios ($\delta^{13}C$) of dissolved inorganic carbon (DIC) and Cd/Ca ratios as recorded by benthic foraminifera. Both proxies vary as a function of nutrient content. Most of our present knowledge on past ocean circulation comes from these tracers, which yield consistent results in most ocean areas. Comparison of benthic $\delta^{13}C$ records from the North Atlantic with various other locations in the Atlantic, Southern Ocean, and Pacific show larger differences during glacial than interglacial periods, which has been attributed to greatly reduced glacial deep water (North Atlantic Deep Water (NADW)) production during the late Pleistocene [*Boyle and Keigwin*, 1982, 1987; *Curry and Lohmann*, 1982; *Charles and Fairbanks*, 1992]. The same result was obtained from the ^{14}C distribution in the deep ocean during the last glacial [*Broecker et al.*, 1990]. During glacials, NADW was replaced by a shallower water mass, Glacial North Atlantic Intermediate Water (GNAIW), which probably supplied smaller volumes of water to the Southern Ocean than NADW during interglacials [*Boyle and Keigwin*, 1987; *Boyle*, 1988; *de Menocal et al.*, 1992; *Oppo and Lehman*, 1993; *Oppo et al.*, 1997; *Marchitto et al.*, 1998; *Oppo and Horowitz*, 2000]. There is evidence for the existence of GNAIW since at least ~1.7 Ma [*Raymo et al.*, 1989; *Ruddiman et al.*, 1989; *Bickert et al.*, 1997; *Mc Intyre et al.*, 1999].

[3] In contrast, unchanged glacial-interglacial Southern Ocean Cd/Ca ratios have suggested that the export of NADW remained more or less unchanged between glacial and interglacial periods [*Boyle*, 1992]. The same conclusion was reached from relatively constant glacial and interglacial $^{231}Pa/^{230}Th$ ratios in Southern Ocean sediments, which were interpreted to reflect similar glacial and interglacial export of ^{231}Pa (and thus NADW export) to the Southern Ocean [*Yu et al.*, 1996]. More recently, it was argued, however, that the Southern Ocean $^{231}Pa/^{230}Th$ ratios are not as sensitive to NADW export as previously thought and can therefore not be used to assess the strength of NADW export quantitatively [*Asmus et al.*, 1999]. In addition, it was later suggested that the uncertainty of the mean Atlantic $^{231}Pa/^{230}Th$ ratios of the Holocene and the LGM is too large to rule out even large changes in NADW export [*Marchal et al.*, 2000].

[4] On longer timescales, it has been suggested that deep water production in the North Atlantic has persisted with some short discontinuities since the mid-Miocene (circa 14 Ma) [*Woodruff and Savin*, 1989; *Wright and Miller*, 1996]. At ~4.6 Ma an increase in intensity of NADW production related to the closure of the Panama gateway was deduced from Carribbean carbon isotope and sand fraction records [*Tiedemann and Franz*, 1997; *Haug and Tiedemann*, 1998]. Production persisted at high intensity during the warm early Pliocene epoch [*Billups et al.*, 1998; *Ravelo and Andreasen*, 2000]. Results of a study of the accumulation history of sediment drifts in the North Atlantic supported a stronger NADW production during the early Pliocene but also suggested that NADW production has remained at overall high values during the following Pleistocene [*Wold*, 1994].

[5] After the onset of NHG at about 3 Ma [*Shackleton et al.*, 1984; *Raymo*, 1994] NADW flow became intermittent, high during interglacials and lower during glacials. A major intensification of

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global thermohaline circulation and increase of NADW production after the onset of Northern Hemisphere glaciation (NHG) was deduced from an increase in grain size in central and South Atlantic Ocean sediments [*Mountain and Tucholke*, 1985; *Turnau and Ledbetter*, 1989]. A potential alternative cause for this grain size signal may, however, have been an increased carbonate dissolution due to a northward advance of more corrosive deep water originating from the Southern Ocean, enabled by a weakening of NADW flow from the north, in particular during cold periods [*Raymo et al.*, 1992]. An overall decrease in NADW production over the past ~3 Myr was deduced from $\delta^{13}C$ comparisons of North Atlantic and Pacific sediments, which show a smaller difference prior to the onset of NHG than afterward [*Raymo et al.*, 1990, 1992; *Raymo*, 1997]. This was confirmed by micropaleontological results which suggest an increase in the influence of southern component water masses in the North Atlantic after 2.9 Ma, indicating a weakening of NADW production [*Ishman*, 1996].

[6] In summary, there appear to be some discrepancies between the geochemical and sedimentological results but also among the different geochemical approaches ($\delta^{13}C$ and Cd/Ca) to reconstruct the strength of thermohaline overturn, NADW production, and export in the Atlantic Ocean. These discrepancies are particularly pronounced in the Southern Ocean and are, in the case of $\delta^{13}C$ and Cd/Ca, probably caused by factors other than nutrient content, such as nonconservative effects of temperature and nutrient availability [*Broecker and Peng*, 1982], carbonate ion concentration [*Spero et al.*, 1997], and high organic carbon accumulation [*Mackensen et al.*, 1993] for $\delta^{13}C$, whereas Cd/Ca has probably been influenced by thermodynamic effects [*Boyle*, 1992]. These uncertainties essentially prevent the use of these proxies for a quantitative assessment of past water mass mixing.

1.2. Radiogenic Isotopes as Water Mass Proxies

[7] Nd and Pb isotope ratios have been shown to be alternative proxy tracers for water masses and have the advantage of being independent of biogenic fractionation processes in the water column. For Nd the only way the isotope composition of a water mass can change is by addition of eolian or riverine inputs with a different isotopic composition or by mixing with other water masses. The average oceanic Nd residence time between ~600 and 2000 years allows the use of Nd isotopes as a quasi-conservative water mass tracer [*Jeandel*, 1993; *Tachikawa et al.*, 1999], in particular in the Atlantic and Southern Oceans, where water mass residence times are short (only few 100 years at maximum). The reason for the distinct Nd isotope composition of water masses, particularly of intermediate and deep waters, is the weathering and dissolution of rocks with different isotope compositions in the source regions of the water masses (Nd isotope ratios are expressed as ε_{Nd} values, which correspond to the measured $^{143}Nd/^{144}Nd$, normalized to the chondritic uniform reservoir (CHUR) (0.512638), multiplied by 10,000). Because of weathering of rocks on the old continental landmasses of the Canadian Shield and Greenland, which have extremely unradiogenic Nd isotope ratios (low ε_{Nd}) [*Stordal and Wasserburg*, 1986], the core of NADW presently has a typical ε_{Nd} value of −13.5, whereas water masses originating from the Atlantic sector of the Southern Ocean have ε_{Nd} values between −7 and −9 as a consequence of mixing between low ε_{Nd} Atlantic and high ε_{Nd} Pacific water masses [*Piepgras and Wasserburg*, 1982, 1987; *Jeandel*, 1993] (see also compilation of these data by *von Blanckenburg* [1999]). Pacific seawater has high ε_{Nd} values between 0 and −6 owing to weathering of young mantle-derived volcanic rocks with high ε_{Nd} values [*Piepgras and Jacobsen*, 1988; *Shimizu et al.*, 1994].

[8] The isotope composition of Pb, which has a much shorter oceanic residence time of 80–100 years, is also a potential water mass tracer for shorter length scales but cannot be measured directly in seawater because of anthropogenic perturbations [*Schaule and Patterson*, 1981]. The bottom water isotope composition of dissolved Nd [*Albarède and Goldstein*, 1992; *Albarède et al.*, 1997] and of preanthropogenic Pb [*Abouchami and Goldstein*, 1995; *von Blanckenburg et al.*, 1996b] has, however, been recorded by ferromanganese crusts and nodules. For Nd it was shown that the isotope composition of ferromanganese nodules and crusts is in equilibrium with the respective ambient deep water masses to within 1 ε_{Nd} unit, where water column data are available, which demonstrates that Nd isotopes and, by inference, also Pb isotopes are not fractionated during incorporation into crusts. The only region where the Nd isotope composition of deep water and crust surfaces does not agree is the western Atlantic sector of the Southern Ocean. There the Nd isotope ratios in the surfaces of crusts and nodules, which integrate over several 100 kyr of growth history, are consistently higher (more Pacific-like) than present-day ambient deep water [*Albarède and Goldstein*, 1992; *Jeandel*, 1993; *Albarède et al.*, 1997]. This may be explained by the integrated effect of decreased glacial NADW contributions to Southern Ocean water masses and therefore stronger influence of Pacific water masses with higher ε_{Nd} during glacials [*Albarède and Goldstein*, 1992; *Albarède et al.*, 1997]. Such a scenario has also been deduced from $\delta^{13}C$ variations in Southern Ocean sediments [*Oppo et al.*, 1990; *Charles and Fairbanks*, 1992] and from a 3–5 ε_{Nd} unit shift to more Pacific-like deep water Nd isotopic composition recorded by Mn coatings of foraminifera in Cape Basin sediments during the last glacial compared with marine isotope stage 3 and the Holocene [*Rutberg et al.*, 2000].

[9] For the past 10 Myr, ferromanganese crusts and nodules can be dated reliably using profiles of the ratio of the radioactive cosmogenic isotope ^{10}Be to stable ^{9}Be. This enables the reconstruction of paleocirculation, water mass distribution, and changes of source provenances of Nd and Pb to the ocean [*Ling et al.*, 1997; *Burton et al.*, 1997, 1999; *Christensen et al.*, 1997; *Abouchami et al.*, 1997; 1999; *Frank and O'Nions*, 1998; *O'Nions et al.*, 1998; *Reynolds et al.*, 1999; *Frank et al.*, 1999b]. Over the past 3 Myr, there has been a major shift toward lower ε_{Nd} and higher $^{206}Pb/^{204}Pb$ within NADW in the NW Atlantic [*Burton et al.*, 1997, 1999; *O'Nions et al.*, 1998; *Reynolds et al.*, 1999], which has mainly been attributed to an increase in the supply of continental weathering products from the old cratonic areas of the Canadian Shield and Greenland [*O'Nions et al.*, 1998; *von Blanckenburg and O'Nions*, 1999; *Reynolds et al.*, 1999; *Vance and Burton*, 1999]. As is the case for $\delta^{13}C$, information on the strength of NADW production and export to other ocean basins can only be recovered by drawing comparisons with data from areas distal to the NADW production sites. The ideal location is the Southern Ocean, where the Nd and Pb isotope signal of NADW is efficiently mixed with water masses of the Antarctic Circumpolar Current (ACC) system to form Circumpolar Deep Water (CDW). In this paper we present the first long-term Nd and high-precision Pb isotope time series obtained from ferromanganese crusts and nodules in the Southern Ocean, which constrain the response of the Southern Ocean water masses to the isotopic variability of NADW over the past 14 Myr.

2. Material and Methods

[10] Five ferromanganese crusts and one nodule from the Southern Ocean were analyzed in this study (Figure 1). Locations, sample depths, and other details are given in Table 1. Crust Atlantis II was recovered from the southern side of the crest of the Walvis Ridge, which at present, corresponds to the boundary between NADW and Upper Circumpolar Deep Water (UCDW). The Cape Basin nodule was recovered from the deep Cape Basin, which is occupied by Lower Circumpolar Deep Water (LCDW). Some major element data and a description of the location and the sedimentary environment in which this nodule grew have been published before [*Rogers*, 1987].

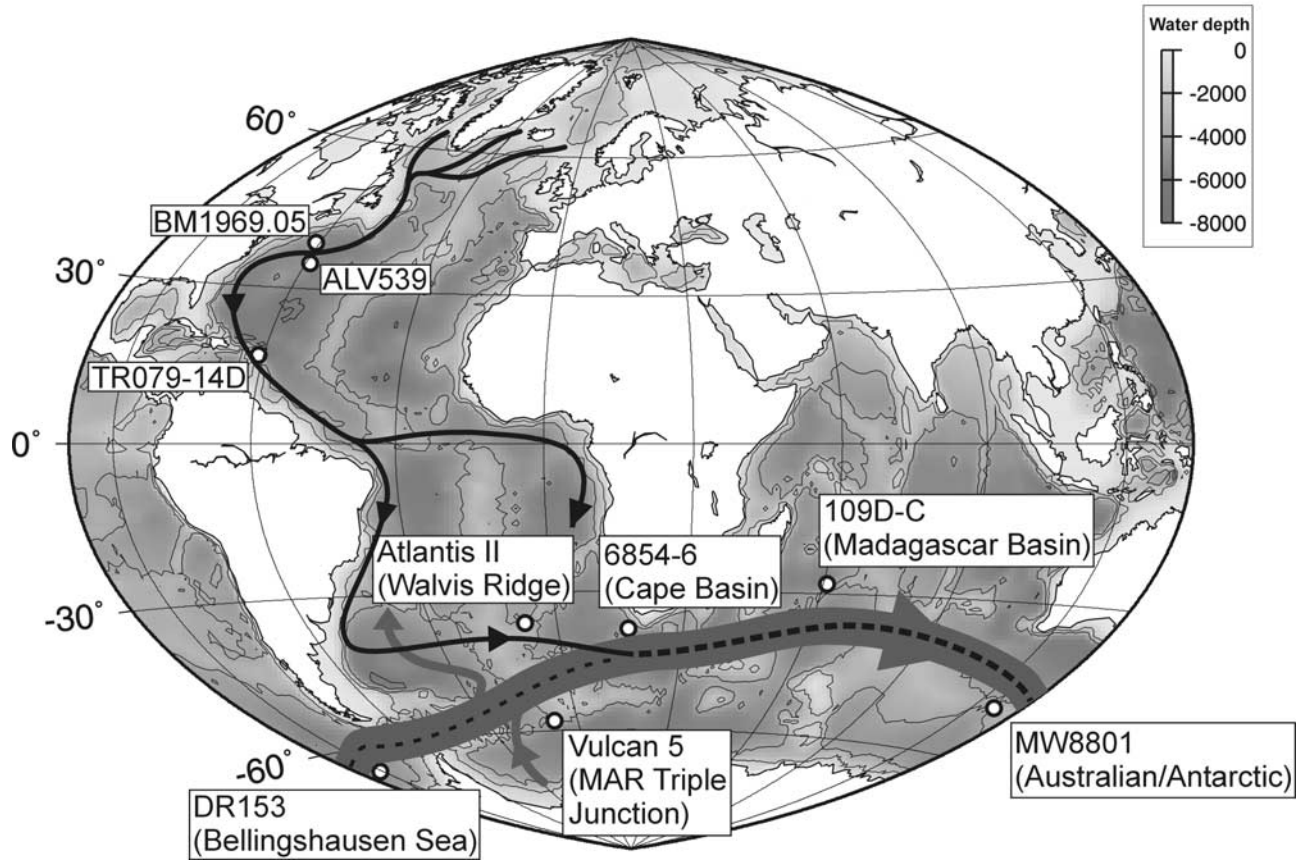

Figure 1. Locations of the investigated crusts of this work in the Southern Ocean and previously published records from the NW Atlantic Ocean [*Burton et al.*, 1997, 1999; *O'Nions et al.*, 1998; *Reynolds et al.*, 1999]. The flow pattern of NADW is shown schematically as solid line. The circulation pattern of the ACC is given as thick shaded line. The thinner shaded line going into the ACC from the south represents the contribution of Weddell Sea Deep Water, and the shaded line leaving the ACC into the Argentine Basin stands for northward flowing LCDW.

Four more records are presented from crusts which have grown from a location within present-day LCDW: Crust Vulcan 5 is from a more southerly location close to the Mid-Atlantic Ridge (MAR) triple junction in the Atlantic sector of the Southern Ocean, crust 109D-C is from the Madagascar Basin, crust MW 8801 is from the SE Indian Ridge between Australia and the Antarctic, and crust DR153 was recovered from a seamount in the Amundsen Abyssal Plain, west of the Drake Passage in the Bellingshausen Sea.

Table 1. Locations and Details of Crusts[a]

Cruise	Sample	Latitude	Longitude	Water Depth, m	Source of Isotope Data		Thickness, mm	Average Growth Rate, mm/Myr	Base Age, Ma
					Nd + Pb	Be			
				Atlantic Ocean (Previously Published)					
-	BM1969.05	39°00′N	60°57′W	1829	1	2	130	1.62	60
ALV 539	2-1	35°36′N	58°47′W	2665	2	2	90	2.37	38
TR079	D-14	16°55′N	61.10′W	2000	3	3	9.5	2.85	3
				Southern Ocean (This Study)					
Antipode	109D-C	27°58′S	60°48′E	5689-5178	2	2	30	1.60	14
Atlantis II	D4-1	36°23′S	7°31′W	2184	-	-	31	1.92	10
Vulcan 5	D34-42	57°47′S	7°40′W	3690–3900	-	-	15	6.14	3
TBD463	6854-6	37°47′S	16°55′E	4517	-	-	33	3.86	7.5
MW8801	D18-1	50°03′S	126°45′E	3993	-	-	15	4.8	3
BAS	DR153u/n	64°58′S	91°16′W	3300-3150	-	-	6	0.7	6.5

[a] Sources of isotope data are 1, *Burton et al.* [1997]; 2, *O'Nions et al.* [1998]; 3, *Reynolds et al.* [1999]. Average growth rates for all crusts and nodules given above have been derived from $^{10}Be/^{9}Be$ ratios. In those cases where the ages of the bases of the crusts given in the base age column exceed 7–8 Ma, the maximum ages were calculated by Co chronometry [*Frank et al.*, 1999a]. Coarse-resolution Pb (conventional low-precision TIMS measurements), Nd, and Be isotope data of crust 109D-C have been published before [*O'Nions et al.*, 1998]. For this study a high-resolution and high-precision (MC-ICPMS) Pb isotope profile has been produced for crust 109D-C.

[11] The $^{10}Be/^{9}Be$ ratios (Figure 2) were measured using the Oxford ISOLAB [*Belshaw et al.*, 1995] employing previously described methods of chemical purification [*von Blanckenburg et al.*, 1995; *O'Nions et al.*, 1998]. Chemical separation and purification methods for Nd and Pb followed those of *Cohen et al.* [1988] and *Galer and O'Nions* [1989]. Nd isotopes were measured by thermal ionization mass spectrometry (TIMS) as described by *Cohen et al.* [1988]. All errors shown on the figures are 2σ external reproducibilities and based on within-run precision for individual mass spectrometer analyses. Here $^{143}Nd/^{144}Nd$ was normalized to $^{146}Nd/^{144}Nd = 0.7219$ to correct for instrumental mass bias. The $\varepsilon_{Nd(T)}$ values were calculated using $^{147}Sm/^{144}Nd = 0.115$. Repeated analysis of the La Jolla Nd standard yielded 0.511838 ± 8 ($n = 33$) for the period of time during which the Cape Basin nodule was measured and 0.511836 ± 6 ($n = 16$) for the period during which the other crusts were measured. All Nd isotope data including those from the previous publications of the NW Atlantic crusts have been normalized to a standard value of 0.511858 for Figure 3 and for all calculations carried out in order to allow direct comparison of all data. The Pb isotope ratios were measured on a Nu Instruments multiple collector inductively coupled plasma mass spectrometer (MC-ICPMS). Applying a Tl-doping procedure, this technique allows the measurement of Pb isotope ratios at a precision which is about an order of magnitude higher than the conventional TIMS techniques [*Belshaw et al.*, 1998; *Reynolds et al.*, 1999; *Frank et al.*, 1999b]. The external reproducibility of the NIST SRM981 Pb standard during the course of this work was $^{206}Pb/^{204}Pb = 16.9296 \pm 34$; $^{207}Pb/^{204}Pb = 15.4831 \pm 31$; $^{208}Pb/^{204}Pb = 36.6745 \pm 73$; $^{207}Pb/^{206}Pb = 0.914585 \pm 89$; $^{208}Pb/^{206}Pb = 2.16630 \pm 17$ ($n = 22$). In-run precision for each sample was better than the external reproducibility. All data are available on request from the corresponding author or electronically at the PANGAEA database.[1]

3. Results

[12] The isotope compositions of Pb, Nd, and Be at the surfaces of the crusts display only a relatively small variability confirming efficient homogenization within the present-day circumpolar Antarctic water masses. The data are fully consistent with the distribution of previously published crust and nodule surface data [*Abouchami and Goldstein*, 1995; *von Blanckenburg et al.*, 1996a; *Albarède et al.*, 1997].

[13] Growth rates of the four new crusts and the Cape Basin nodule derived from the $^{10}Be/^{9}Be$ profiles (Figure 2) vary between 0.7 and 6.14 mm/Ma, which is typical for hydrogenetic ferromanganese crusts. All surfaces show similar $^{10}Be/^{9}Be$ ratios close to 1×10^{-7}, which corroborates that they all correspond to present growth surfaces. One of the crusts is older than 7–8 Ma (Atlantis II) and can therefore not be dated with $^{10}Be/^{9}Be$ in the older part. For this crust a Co concentration profile was measured by electron probe to determine independent growth rates [*Manheim*, 1986; *Frank et al.*, 1999a]. The Co data indicate that the average growth rate obtained from $^{10}Be/^{9}Be$ cannot simply be extrapolated to the base of the crust because growth rates were higher in the older part below 16 mm depth. The Co-growth rate relationship of *Manheim* [1986] was calibrated to match the $^{10}Be/^{9}Be$-derived growth rate in the upper part of this crust, which results in an age of 10 Ma at the base of the crust at 31 mm depth (Figure 2).

[14] None of the six crusts and nodules shows any significant variability in Nd isotope composition over the past 14 Myr, with the possible exception of a slight trend toward higher ε_{Nd} over the past 3–5 Myr in the Cape Basin nodule record (Figure 3a). In contrast, the high-precision Pb isotope data for these crusts and nodules show clearly resolvable trends (Figure 3b). The Atlantis II and Bellingshausen Sea crusts exhibit step-like trends toward more Pacific-like Pb isotope ratios over the past 10 Myr. The Pb isotope ratios of crusts 109D-C and the Cape Basin nodule did not vary greatly prior to 3–4 Ma, but since then, the Pb isotope ratios in these two crusts and Vulcan 5 have also become progressively more Pacific-like. Thus the slight trend in Nd isotopes and the pronounced changes in Pb isotopes in five of the six crusts are exactly opposite to the trends observed for NADW in the NW Atlantic (Figure 3). The Pb isotope record of the crust from south of Australia is the only exception as it displays the opposite trend. This crust was recovered close to the mid-ocean ridge, and there is evidence for hydrothermal influences, which may have affected the Pb isotope record.

[15] In order to show that a reliable record of ambient deep water isotope composition, unaffected by diagenetic contributions from the sediment pore waters, was obtained for the Cape Basin nodule, Nd and Pb isotope profiles were measured from the top side and the bottom side, which grew in contact with the sediment surface. The records shown in Figure 3 are indistinguishable, even within the small analytical uncertainties of the high-precision Pb isotope measurements and confirm that the isotope data indeed represent past deep water isotope composition.

4. Discussion

[16] It might be argued that the missing reflection of the isotope variations observed in NADW in the NW Atlantic in the Southern Ocean suggests that the Nd and Pb isotope signal has simply not been transferred to the Southern Ocean but has been mixed and removed within the Atlantic Ocean before it arrived in the Southern Ocean. This is, however, unlikely for several reasons. In the present-day Atlantic the advection of the Nd isotope signature of NADW into the Southern Ocean is well supported by water column data [*Piepgras and Wasserburg*, 1982, 1987; *Jeandel*, 1993]. In addition, there is evidence from surface data of ferromanganese crusts and nodules that the Nd and Pb isotope signatures of NADW are traceable at least until the eastern Atlantic sector of the Southern Ocean [*Albarède and Goldstein*, 1992; *Albarède et al.*, 1997; *Abouchami and Goldstein*, 1995]. Water column ^{14}C data suggest that the ventilation time of the deep western Atlantic is on the order of 100 years [*Broecker*, 1979] and that the deep water replacement time for the entire Atlantic Ocean is on the order of 275 years [*Stuiver et al.*, 1983]. Compared with the average residence times of Nd and Pb, this means that most of the Nd and at least some of the Pb contained in NADW in the NW Atlantic is exported to the Southern Ocean. This is supported by the observation that ~50% of the ^{231}Pa produced in the Atlantic are currently exported to the Southern Ocean via NADW [*Yu et al.*, 1996]. The average ocean residence time of particle-reactive ^{231}Pa is of the order of 100 years and thus very similar to that of Pb.

[17] Thus the much more likely explanation for the Southern Ocean isotope records is an overall decrease of the input of NADW into the ACC over the past ~3–4 Myr. In support of this, the Pb isotope data of the Southern Ocean crusts and nodules define approximate binary mixing lines between unradiogenic (southern component water (SCW)) and radiogenic (northern component water (NCW), NADW) end-members for the past 3–4 Myr (Figure 4), which trend toward the SCW end-members with time. Similarly, binary mixing lines are observed for the NW Atlantic Pb isotope data for the same period, but there the trends are toward the NCW end-member with time. This suggests a continuous decrease of the export of NADW to the Southern Ocean over the past 3–4 Myr. If Pb was a conservative tracer in the ocean and if all the binary mixing lines fell on the same general mixing line, it

[1] Supporting data are available electronically from the Pangaea database, Alfred-Wegener-Institut für Polar- und Meeresforschung, Columbusstrasse, 27568 Bremerhaven, Germany, (email: info@pangaea.de; http://www.pangaea.de).

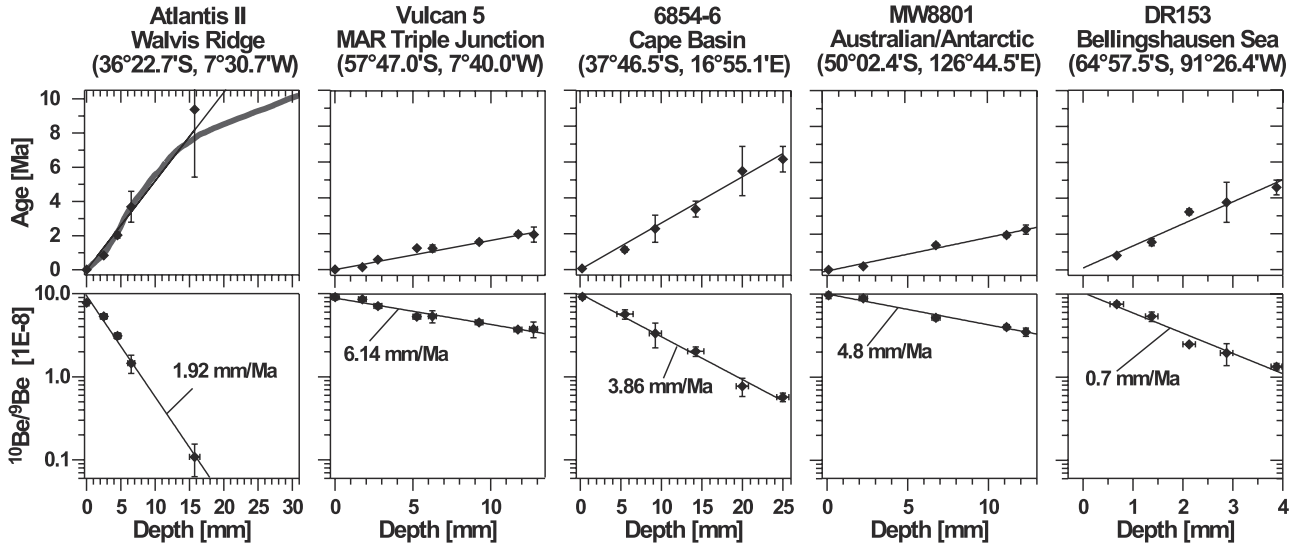

Figure 2. The $^{10}Be/^{9}Be$ ratios in crusts Atlantis II, Vulcan 5, the Cape Basin nodule, MW8801, and DR153 versus depth beneath the growth surface. The ages have been calculated with a half-life for ^{10}Be of 1.5 Myr and assuming a constant initial $^{10}Be/^{9}Be$ ratio. The growth rates and ages beyond the age range covered by $^{10}Be/^{9}Be$ data for crust Atlantis II have been calculated using a Co-growth rate relationship [*Manheim*, 1986] which was calibrated to match the $^{10}Be/^{9}Be$ dating of the younger part (shaded line).

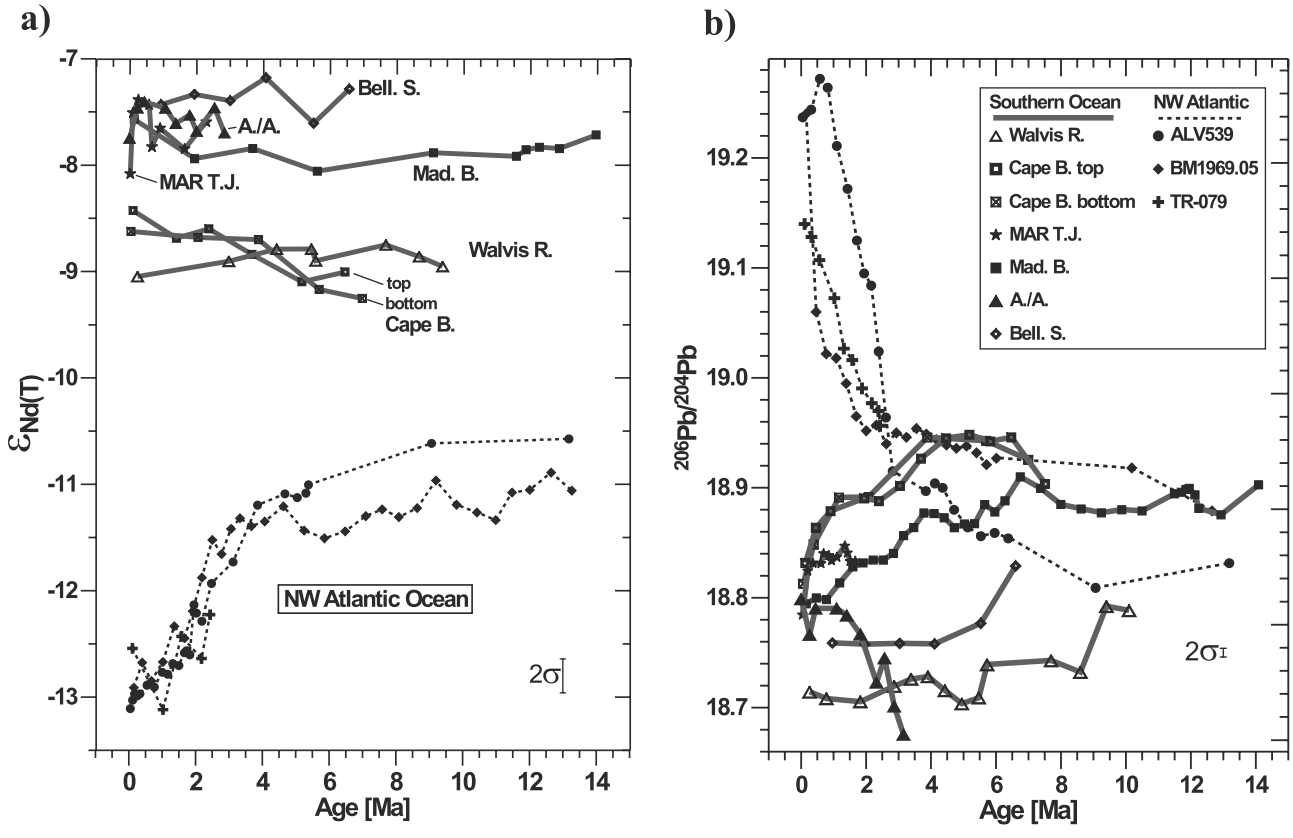

Figure 3. Time series of $\varepsilon_{Nd(T)}$ and $^{206}Pb/^{204}Pb$ versus age derived from $^{10}Be/^{9}Be$ dating (Figure 2) for the Southern Ocean crusts plotted as thick shaded lines (open triangles, Walvis Ridge; open squares, Cape Basin top profile; crossed squares, Cape Basin bottom profile; solid squares, Madagascar Basin; solid stars, MAR triple junction; solid triangles, Australian/Antarctic; open diamonds, Bellingshausen Sea). The isotope time series from the NW Atlantic crusts (dashed lines) which have grown from NADW are shown for comparison [*Burton et al.*, 1997, 1999; *O'Nions et al.*, 1998; *Reynolds et al.*, 1999] (solid circles, ALV539; solid diamonds, crust BM1969.05; crosses, TR-079).

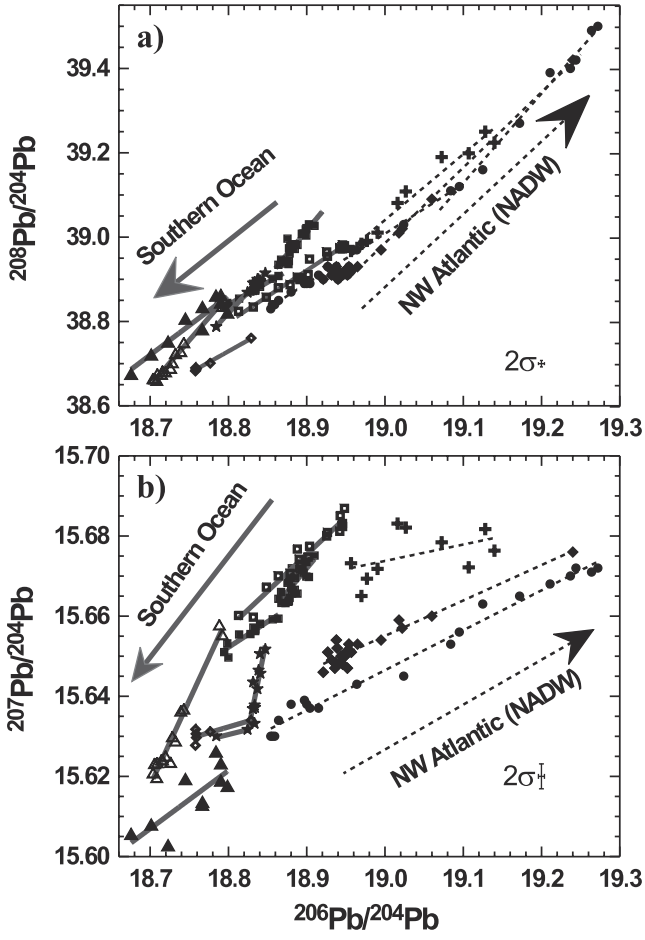

Figure 4. Comparison of Pb isotopes in $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ space. Symbols are the same as in Figure 3. The shaded arrow indicates the trends with time of the mixing lines for all crusts from the Southern Ocean except the Australian/Antarctic area, whereas the NW Atlantic trend is shown by a dashed arrow. Error bars represent 2σ external reproducibilities.

would be possible to quantify the varying proportions of the two end-members forming CDW from the Pb isotopes. Pb is, however, quite strongly particle reactive and therefore not conservative, which means that the isotopic signature at any given location in the ocean is a complex mixture of advected water mass signals and local weathering derived signals. This is mirrored by the fact that the Pb isotope mixing lines of the different NW Atlantic and Southern Ocean crusts are not collinear, demonstrating that local contributions play an important role (see particularly Figure 4b). The importance of local contributions for Pb isotopes is also documented by the trend opposite to all others in the record from south of Australia and by the fact that the Pb isotope data of crust Atlantis II, which has grown closest to the sites of NADW production, shows the largest difference from the Pb isotope data of NADW in the NW Atlantic (Figure 3b). Thus the observations from five of the six Pb isotope time series are consistent with a diminishing NADW input into the Southern Ocean over the past few million years, but local contributions prevent any quantitative estimates.

[18] In contrast, owing to the much lower particle reactivity and thus longer residence time of Nd compared with Pb, Nd isotopes provide a suitable proxy tracer for water mass composition and mixing in the past, which is at least semiquantitative. This view is supported by the fact that those Nd isotope records located nearest to the sources downstream of NADW have retained a Nd isotope signature which is most similar to the NADW Nd isotope composition in the NW Atlantic. With increasing distance from the sources the Nd isotope data in the Southern Ocean have become more Pacific-like, which is consistent with the oceanographic evidence and the previously published Nd data on crust and nodule surfaces [*Albarède and Goldstein*, 1992; *Albarède et al.*, 1997].

[19] The Nd isotope composition of NADW as recorded in the NW Atlantic has decreased over the past ~3 Myr while Southern Ocean water masses have remained constant, which indicates a general reduction of NADW export into the Southern Ocean accompanied by a simultaneous decrease of ε_{Nd} within NADW over time. This may appear coincidental but is explainable by the substantial consequences of the onset of NHG for the style of weathering on the continents and at the same time also for ocean circulation (see section 1). The strength of NADW export from the locations of the previously published crusts in the NW Atlantic to the Southern Ocean over the past 3.5 Myr is calculated by simple mass balance between the Nd isotope values in the NW Atlantic and the Southern Ocean (Table 2). For the present NADW in the NW Atlantic, a Nd isotope composition of −13 ε_{Nd} units is applied [*Piepgras and Wasserburg*, 1982, 1987; *Jeandel*, 1993]. Assuming zero NADW contribution, the Pacific-like SCW end-member values range between −4 and −6 ε_{Nd} units, similar to the last glacial Nd isotope values found in Cape Basin sediments [*Rutberg et al.*, 2000]. A linear mixing relationship for Nd between the two end-member water masses is assumed because the concentrations of Nd in NADW and CDW do not show a clear systematic difference [*Piepgras and Wasserburg*, 1987; *Jeandel*, 1993], although NADW tends to be overall somewhat lower. If this small difference is considered systematic, the results of the calculations below represent maximum estimates.

[20] For the present-day ocean these mass balance calculations suggest that depending on the value chosen for the southern component water mass end-member, between 35 and 56% of the waters at the location of crust Atlantis II and the Cape Basin nodule are composed of NADW. For these locations the mixing proportions are in reasonable agreement with previous estimates based on oceanographic data [*Broecker*, 1979; *Döös*, 1995] (see also model-derived estimates of Döös given by *Albarède et al.* [1997]) and estimates based on water column Nd isotope data [*Piepgras and Wasserburg*, 1987; *Jeandel*, 1993]. For the locations of the other crusts farther away from the NADW sources the amount of NADW is calculated to be 25–40%, which is explained by mixing with larger volumes of southern component water masses, ultimately of Pacific origin. Comparison of the Nd isotope data at 1.5 and 3.5 Ma suggests that the overall contribution of NADW to water masses at the Walvis Ridge decreased by 14–18% from 3.5 Ma to the present. An even stronger relative decrease of 24–37% is calculated for the deeper crusts and nodules, which represent LCDW.

[21] Rather than an overall decrease of NADW export with time, the data may alternatively be explained by an evolution of more pronounced glacial periods since the onset of NHG, during which NADW export became weaker and was replaced by GNAIW. This would result in the same patterns of the Nd isotope records given that the individual crust samples integrate over several glacial-interglacial cycles. Indeed, some of the long-term carbon isotope records suggest such a gradual increase in the strength of the glacial periods, in particular, over the past 1 Myr [*Raymo et al.*, 1989, 1990]. This may also explain why the relatively shallow location of crust Atlantis II on the Walvis Ridge at only 2200 m

Table 2. Reconstruction of NADW Export to the Southern Ocean

Age, Ma	NW Atlantic[a]	Southern Ocean[a]	Difference to NW Atlantic[b]	Percent NADW[c]	Percent Relative Decrease of NADW Since 3.5 Ma[c]
			Atlantis II (Walvis Ridge)		
3.5	−11.5	−8.9	2.6	53–65	-
1.5	−12.3	−9.0	3.3	47–60	8–11
Present	−13	−9.1	4.0	44–56	14–18
			6854-6 (Cape Basin nodule)		
3.5	−11.5	−8.8	2.3	52–65	-
1.5	−12.3	−8.7	3.2	43–57	13–18
Present	−13	−8.4	4.2	35–49	24–33
			109D-C (Madagascar Basin)		
3.5	−11.5	−8	3.5	36–53	-
1.5	−12.3	−7.8	4.5	29–46	14–21
Present	−13	−7.6	5.4	23–40	25–37

[a] Data are $\varepsilon_{Nd(T)}$ values.
[b] Data are ε_{Nd} values.
[c] Numbers are percentages of NADW calculated with Pacific water mass end-member ε_{Nd} values of −6 and −4 similar to recent results obtained for last glacial Nd isotope compositions in the Atlantic sector of the Southern Ocean [*Rutberg et al.*, 2000]. Calculations for the remaining crusts farther downstream within LCDW give results similar to the Madagascar Basin.

water depth, relatively far north in the southern Atlantic, indicates a smaller relative decrease in NADW export over the past 3 Myr. It may have received some GNAIW contributions during the glacial periods [*Oppo and Horowitz*, 2000], whereas the locations of the other deeper crusts were not reached by this shallower water mass with its low ε_{Nd} signature during glacials.

[22] On longer timescales, between 3 and ∼14 Ma, the Nd isotope data suggest that there was not only a strong and continuous export of NADW or a precursor of it to the Southern Ocean since the early Pliocene but for this entire period, which is in agreement with previous results obtained from carbon isotope records [*Woodruff and Savin*, 1989; *Wright and Miller*, 1996].

[23] It might be argued that the variability of the Nd and Pb isotope composition of NADW exported to the Southern Ocean over the past 3 Myr has been compensated by a concomitent change of the isotopic composition of SCW, thus not requiring a change of mixing proportions. Such a change may have been caused by variations of the weathering inputs from the Antarctic continent, which may have changed the Nd and Pb isotope composition of deep water produced around the Antarctic and which has been mixed with NADW to form CDW. However, ε_{Nd} values of roughly −2 to −3 and Pb isotope ratios of 18.2–18.3 which would be necessary for such a compensation appear to be unrealistic. There are not many isotope data available for continental rocks from the Antarctic continent, but they are generally unlikely sources of such Nd and Pb isotope signatures. In addition, significant overall changes of weathering inputs and deep water production over the past 3 Myr are also considered unlikely owing to the persisting Antarctic glaciation over the last ∼14 Myr, which suggests quite stable environmental and climatic conditions.

[24] It might further be argued that a 14–37% reduction in NADW export to the ACC should be visible in an increase of the $^{10}Be/^{9}Be$ ratio in CDW over the past 3 Myr. Calculating the same mass balance as above for $^{10}Be/^{9}Be$ with a NW Atlantic NADW end-member value of 0.4×10^{-7}, a present-day CDW value of 1.0×10^{-7}, and a Pacific-like southern component end-member of 1.4×10^{-7} [*von Blanckenburg et al.*, 1996a], the resulting effect of the reduced NADW input for CDW is in the range of $0.06–0.12 \times 10^{-7}$. Such a small effect is not resolvable with the current statistical uncertainties of the Be isotope measurements.

[25] Finally, the radiogenic isotope time series obtained for the Southern Ocean also have implications for the interpretation of the Pb and Nd isotope evolution of the deep Pacific Ocean. It was speculated that a 0.5 ε_{Nd} unit decrease in the Nd isotope composition over the past 3–5 Myr found in records obtained from ferromanganese crusts [*Ling et al.*, 1997] and fish teeth [*Martin and Haley*, 2000] in the equatorial and NW Pacific Ocean was caused by an intensification of NADW production and thus a transfer of the NW Atlantic NADW signature to the deep Pacific. The evidence for a decrease in NADW export presented in this study and the patterns of the Pb and Nd isotope composition in the deep Southern Ocean itself exclude this possibility and clearly demonstrate that the Nd and Pb isotope variability in the deep Pacific Ocean must have been caused by processes within the Pacific basin, such as island arc weathering or aeolian input [*Frank et al.*, 1999b], or variations in the inflow of Southern Ocean water masses [*Abouchami et al.*, 1997].

5. Conclusions

[26] Comparison of Nd isotope data derived from NADW in the NW Atlantic Ocean and Southern Ocean water masses show that the onset of Northern Hemisphere glaciation at ∼3 Ma did not coincide with an overall increase in NADW export but a substantial decrease. Mass balance calculations carried out with these Nd isotope data suggest that averaged over the past several ten thousand years, the overall NADW export was between 14 and 37% lower than at 3.5 Ma. Prior to 3.5 Ma back until 14 Ma, the Nd isotope data indicate a strong overall export of NADW or a precursor of it. These conclusions, derived from several millimeters to a few centimeters of ferromanganese crusts, are not only consistent with carbon isotope results obtained from hundreds of meters of marine sediments but complement these results because they can be used for at least semiquantitative assessment of past water mass mixing. This confirms the value of Nd isotopes as proxy tracer of past ocean circulation and water mass exchange. With the advance of the possibility to extract the deep water Nd isotope composition from marine sediments the Nd isotope water mass proxy will reach its full potential.

[27] Pb isotope data also indicate a decrease in NADW export, but any quantitative estimates are prevented by superimposed local contributions to the dissolved Pb isotope signal of water masses, which suggests that Pb isotopes are more suitable to trace imprints

of local changes in weathering regimes and detrital inputs and small-scale mixing of water masses.

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